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Study of aqueous chemical forms of silicon in organic-rich waters

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Abstract

The study of silicon species in organic-rich waters is a very significant problem. This type of waters is widely spread all over the world. It is characterized by a high content of humic substances, high color of water and low pH. In this regard, a certain determination of silicon concentration in this type of waters is impossible without a preliminary investigation of silicon species. The aim of this research is therefore an investigation of the ratio of silicon dissolved forms in organic-rich waters depending on the silicon concentration and the acidity of the water. The study of pH influence on silicic acids and a silicon–humic matter interaction was carried out using model solutions and natural bog waters (Tomsk region). It has been found that the degree of polymerization of silicic acids essentially depends on the acidity of a solution. Scanning of spectrophotometric measurements has shown that silicon does not form stable complexes with fulvic and humic acids in weak-acid media (pH 3-4). Studying the bog waters of Tomsk Region has shown that they (pH=3.66-3.80) contain only monomeric-dimeric and polymeric forms of silicic acids.

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Keywords: silicon, silicic acids, aqueous silicon forms, organic-rich waters, Tomsk region, molecular spectrophotometry, atomic absorption spectrometry.

1. Introduction

Natural water enriched with silicon occurs as a result of alumosilicate rock weathering, destruction of vegetal

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and animal remains etc. According to [1], silicon forms a lot of various chemical species and can exist in suspended (coarse dispersed), colloid (dispersed) and dissolved forms in natural waters. The dominating species of silicon in natural water is a molecular dispersed species such as orthosilicic acid (H_4SiO_4) [2]. Besides, orthosilicic acid, metasilicic acid (H_2SiO_3) and dimeric forms of these acids ($H_2Si_2O_5$ и $H_{10}Si_2O_9$) can be present in natural waters. Silicic acids are unstable in water solutions. Polycondensation of silicic acids occurs due to the reactivity of silanol groups (Si-OH) [3]. The first stage of this reaction can be described as follows:

$$2H_4SiO_4 \leftrightarrow (HO)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O.$$

Different polysilicic acids having linear and branched structures and molar weight up to 100000-150000 can be formed as a result of polycondensation.

The investigation results of silicon species in different natural conditions are presented in numerous works [4-10]. When studying silicon species in soil solutions, authors[4] identify monosilicic acid, its oligomers and low-molecular and high-molecular polysilicic acids. It is proved that any water solid phase system has equilibrium between monomers and polymers of silicic acid, which is set with the formation of intermediate and unstable low-molecular polysilicic acids.

According to [5], forms of silicic acids with an organic matter can be found in natural waters along with monomeric-dimeric and polymeric species. Among soluble silicon-organic substances in natural waters, the compounds of silicic acids with humic and fulvic acids are significant. Herewith, according to [6,7] stable compounds of silicic asids with humic acids are formed by a donor-acceptor mechanism, while with fulvic acids due to hydrogen bonds. Similar silicon-organic compounds formed by silicic acids and humic acids interaction has been found by [8].

Sometimes colloid particles and gels of silicic acids are put into soluble compounds of silicon[9,10]. As colloids are neither solid nor soluble forms of silicon their study and quantitative analysis require using different approaches and methods.

Despite an increased interest in silicon as a biologically significant element, the problem of ratio of various species of silicon in natural waters and the influence of physicochemical characteristics (particularly pH) and silicon concentration on its polymerization conditions in water solution is disputable up to date.

The study of silicon species in organic-rich waters is a very important problem. This type of waters is widely spread all over the world. It is characterized by a high content of humic substances, high color of water and low pH. In this regard, a certain determination of silicon concentration in this type of waters is impossible without preliminary investigation of silicon species.

So the aim of this research is an investigation of the ratio of silicon dissolved forms in organic-rich waters, depending on silicon concentration and acidity of the water.

2. Methods

The study of pH influence on silicic acids and a silicon–humic matter interaction was carried out using model solutions and natural bog waters (Tomsk region). The model solutions were prepared using sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) and distilled water. Organic substances for experiments were extracted from Tomsk region peats according to I.V. Turine method modified by V.V. Ponomarev and T.A. Plotnikov[11]. Five types of model solutions were prepared. The first model solution with silicon concentration of 20 mg/L was prepared for the investigation of pH influence on silicon forms. pH value was established between 1-12 using 0.1 M HCl and 0.1 M NaOH solutions. The other model solutions were prepared for investigation of silicon–humic matter interaction. Silicon concentrations in the model solutions (from 2 to 5) were 5, 10, 20 и 40 mg/L respectively. An organic substance was added in each solution in amounts corresponding to the organic matter concentration in Tomsk region bog waters. The fulvic acid concentration was 20 mg/L and the humic acid concentration was 5 mg/L in all the solutions. The pH value in the model solutions were kept at 3.6.

Two different methods were used for determination of silicon concentration in various species in model solutions. Silicon concentration in monomeric-dimeric forms as a yellow silicon molybdenum complex was determined by molecular spectrophotometry (SP)[12] (Spekol 21, Germany; Unico 2100, the USA). The total silicon concentration was determined by atomic absorption spectrometry (AAS) (MGA-915, Russia)[13,14]. Besides, the total silicon concentration in natural bog waters was also determined by spectrophotometry. In this case, a preliminary sample preparation such as boiling with NaOH (0.5 mol/l) for destruction of polymeric forms of silicon was done. Humus acids (humic and fulvic acids) contents in a model solution were determined using a titrimetry method[15].

Studying the silicon-humus acids complexes in model solutions was carried out using scanning spectrophotometer SP-56 (Spectr, Russia).

The study of silicon forms in natural rich-organic waters was carried out by example of the bog waters of Bakchar area of Tomsk region. Water sampling was carried out in November, 2013. The bog waters were filtrated using membrane filters (acetyl cellulose) with a pore size of 0.45 and 0.001 μm for the investigation of silicon forms in natural waters. The pH values of the natural bog waters were measured using a water test *in situ.* The main ions (SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+) in natural bog waters were analyzed by ion chromatography (ICS 1000 and ICS 2000), CO_2, CO_3^{2-}, HCO_3^- by titration.

3. Results and discussion

A comparative study of the silicon concentration in the first model solution with different pH was carried out in order to identify pH influence on silicon forms in a water solution. Molecular spectrophotometry (SP) and atomic absorption spectrometry were used.

The silicon concentration determined by SP method in a model solution with pH of 1-9 is much less than that determined by AAS method (Fig. 1). These different results can be explained by the presence of polymer forms of silicic acid not detected by spectrometry. The greatest difference of silicon concentrations detected by both methods is observed in the solution with low pH (pH<5). According to [16], the rate of silicon acid polymerization increases with the growth of hydrogen ion concentration. In the solution with pH>10 the silicon concentration measured by both methods SP and AAS is the same as initial one (20±2.2 mg/L). It is an evidence of the presence of monomeric and dimeric forms of silicic acid and products of its dissociation.

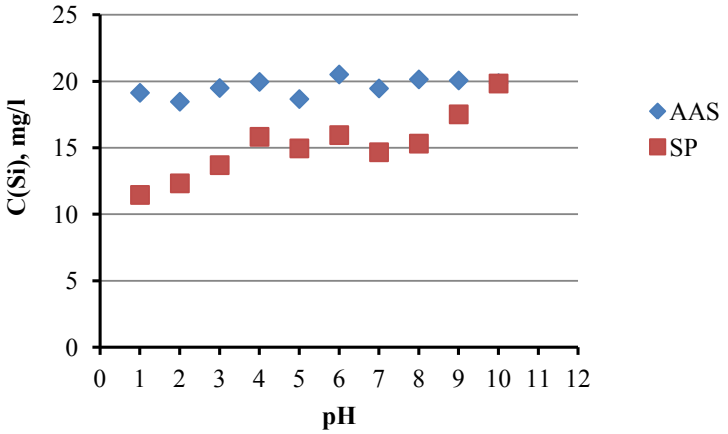

Fig. 1. Silicon concentration in model solution deretmined by SP and AAS vs. pH

As is well known, the bog waters are characterized by low pH values among natural waters. These waters have a brown color and high organic matter concentration. In this context, determining the silicon concentration in the bog waters is necessary to consider the probability of formation of polysilicic acids and silicon and organic matter complexes.

So the study of the silicon concentration in 2, 3, 4, 5 model solutions was carried out using both SP and AAS methods. The results are given in Table 1.

Table 1. Silicon concentration in model solutions (pH=3.6; n = 3; P = 0.95)

Model solution number	Initial silicon concentration, mg/L	Measured silicon concentration, mg/L	
		SP	AAS
2	5	3.2±0.3	5.1±0.5

3	10	6.2±0.6	10.1±1.1
4	20	13.2±1.2	20.0±2.0
5	40	27.8±2.4	39±4

According to the results in Table 1, silicon concentrations determined by AAS method are higher by 30-40 % than silicon concentrations measured by SP method. It can be resulted from the formation of both polymeric silicic acid forms and silicon and organic matter complexes, which have not been detected by SP method.

In order to study the nature of interactions between humic substances and silicic acid, absorption spectra of model solutions in the UV and visible range (200-700 nm) were obtained. The results given in Fig.2 are evidences of the presence of HS absorption band (220 nm) in the absorption spectra of model solutions.

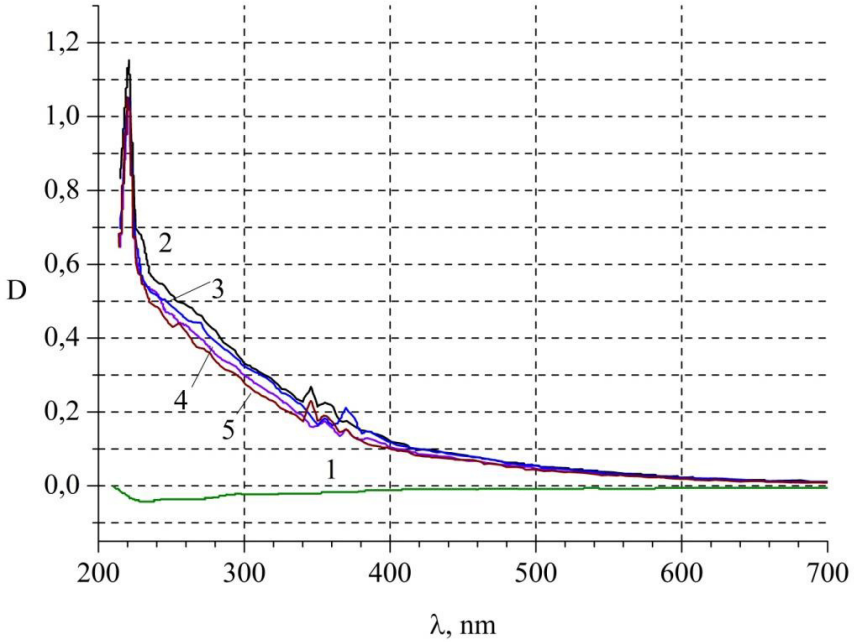

Fig. 2. Absorption spectra of model silicon-HS solutions: 1– model solution with silicon content of 10 mg/l, 2 – model solution of humic substances, FA concentration = 20 mg/l, HA = 5 mg/l; 3 – model solution 2, 4 – model solution 4, 5 – model solution 5.

As we do not observe neither a decrease in the intensity of this band nor appearance of new bands, we can assume stable complex compounds of silicic acid and HS to be absent under these conditions.

Environmental conditions are often very far from those of model experiments. In this context, forms of migration (occurence) of silicon compounds in bog waters located in Bakchar District of Tomsk Region have been investigated. The chemical composition of 7 samples of bog waters collected in November 2013 is presented in Table 2. The examined bog waters are an acid with pH of 3.66-3.80. Waters are ultra fresh, the TDS of waters varies from 30 to 45 mg/l. Sulfate-ion prevails over anions in a chemical composition. It should be noted that an inorganic carbon form prevailing at such low pH values is carbonic acid, the dissociation product of which is CO_2. The concentration of the latter in the examined waters is from 54 to 62 mg/l. Calcium prevailes over cations. The concentration of organic acids in the waters is very high and is of 91.44-113.09 mg/l and 3-4.8 mg/l for fulvic (FA) and humic acids (HA), respectively.

Table 2. Chemical composition of bog waters

Sampling point	pH	TDS, mg/l	Concentration, mg/l									
			CO_2	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	FA	HA
Bog No.1	3.66	30.56	68.60	<3.00	11.80	2.24	6.00	1.22	0.35	0.37	105.01	4.87
Bog No.2	3.72	45.54	60.30	<3.00	27.00	2.08	5.60	1.46	0.35	0.75	113.09	4.87
Bog No.3	3.75	35.99	66.00	<3.00	19.17	2.02	6.00	1.22	0.40	0.43	107.91	3.89
Bog No.4	3.72	35.18	57.20	<3.00	16.00	2.24	6.00	1.22	0.39	0.36	91.44	3.08
Bog No.5	3.75	40.66	61.6	<3.00	23.40	2.35	4.40	1.22	0.79	0.86	100.33	4.10
Bog No.6	3.80	29.40	5.37	<3.00	12.20	2.02	5.00	1.22	0.45	0.44	98.47	3.08

The silicon concentration of monomeric, dimeric or oligomeric forms of silicic acid in bog waters was determined using SP method. The total silicon concentration was determined by AAS and SP methods using preliminary sample treatment (boiling water with NaOH)[12]. The fraction of silicon polymeric forms was estimated by the difference between two determinations points (Table 3, 4).

Table 3. Results on the determination of silicon in the bog waters of Tomsk region using SP and AAS methods

Water sampling point	Concentration of silicon compounds, mg/l				
	SP			AAS	
	Without sample preparation	NaOH treatment	Total	Membrane separation	
				0.45 μ	0.001 μ
1	2	3	4	5	8
Bog No.1	2.7±0.3	5.1±0.5	5.0±0.5	2.6±0.3	3.1±0.3
Bog No.2	3.3±0.4	5.5±0.6	5.5±0.5	3.2±0.3	3.4±0.3
Bog No.3	2.3±0.3	3.9±0.4	4.0±0.4	2.7±0.3	2.7±0.2
Bog No.4	2.7±0.31	4.6±0.5	5.2±0.5	2.8±0.3	3.2±0.3
Bog No.5	3.3±0.4	4.8±0.5	4.6±0.5	3.0±0.3	3.0±0.3
Bog No.6	3.1±0.3	5.0±0.5	5.3±0.5	3.0±0.3	3.3±0.3

As shown in Table 4, the total silicon concentration in bog waters is 4.0-5.3 mg/l. The silicon concentration determined using AAS and SP methods accompanied with NaOH pretreatment coincides within the limits of accuracy. It means that all the dissolved silicon in the examined waters is present only in monomeric-dimeric and polymeric forms of silicic acids. Silicon complexes with organic acids are therefore absent in the waters. Supposedly, the high concentration of hydrogen ions in the bog waters accelerates the processes of silicic acid polymerization and impedes the formation of their complexes with HS containing subacid carboxyl and phenol hydroxyl functional groups[19].

When comparing the results of determination of the silicon concentration in bog waters by SP method without a sample preparation and AAS method, a significant difference that allows estimating the silicon ratio in the form of monomeric-dimeric, oligomeric (their sum) and polymeric silicic acids can be remarked.

According to the analysis of table 4, the examined bog waters are characterized by an approximately equal ratio of monomeric-dimeric, oligomeric (53-69 %) and polymeric (40-47 %) forms of silicic acids. The ratio between the monomer-dimer and oligomer forms increases in point No.5. These results have been validated when studying the ratio between the forms of silicic acids with a different degree of polymerization in bog waters using a membrane separation method. The results are given in Table 3.

Table 4. Ratio of silicic acids forms in bog waters of Tomsk Region

Sampling point	Form of silicon			
	Monomeric-dimeric and oligomeric silicic acids		Polymeric silicic acids	
	mg/l	%	mg/l	%
Bog No.1	2.7	53	2.35	47

Bog No.2	3.3	60	2.27	40
Bog No.3	2.3	59	1.39	41
Bog No.4	2.7	59	2.18	41
Bog No.5	3.3	69	1.45	31
Bog No.6	3.1	62	2.08	38

Taking into account the ratios presented in Table 1 and literature data[18], silicon in the examined bog waters is in the coarse-grained form (the particle size more than 0.45 μ) and in the true dissolved form (the particle size of 0.001 μ) that corresponds to monomer-dimer, oligomer and high molecular weight polymer forms. Colloidal forms of silicon are completely absent in the bog waters.

Conclusions

1. It has been found that the degree of polymerization of cilicic acids essentially depends on the acidity of a solution. The highest rate of the polymerization process catalyzed by hydrogen ions is observed in the acid medium (pH=2-4) and reaches 30-40 %. Formation of anion polymeric forms of silicic acids is intensified by hydroxyl-ions in an alkalescent medium (pH 7-8).
2. Scanning spectrophotometric measurements has shown that silicon does not form stable complexes with fulvic and humic acids in weak-acid media (pH 3-4). On the one hand, the acid medium mitigates dissociation of weak-acid functional groups of humic substances and impedes the formation of complexes. On the other hand, it intensifies the process of polymerization of silicic acids.
3. The study of different forms of silicon in the bog waters of Tomsk Region was carried out. It shows that the acid bog waters (pH=3.66-3.80) enriched in humic substances contain only monomeric-dimeric and polymeric forms of silicic acids. The results of the study have validated that they do not contain complexes if silicon and HS.
4. The fraction (%) of silicic acid polymeric forms was estimated by comparison of the results of the silicon determination using SP and AAS methods. This value reaches 40-47%. Coarse-grained forms of silicon were found using membrane separation (the particle size is more than 0.45).
5. The SP method with a preliminary alkaline sample preparation for destruction of polymeric forms of silicic acids can be used for the determination of silicon in acid bog waters. The AAS method without a sample preparation is also suitable.

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